Fast liquid crystal elastomer swims into the dark

Miguel Camacho-Lopez[*‡], Heino Finkelmann[†], Peter Palffy-Muhoray[‡] and Michael Shelley[§].

[*] School of Physics and Astronomy, University of St. Andrews, St. Andrews, KY16 9SS, Scotland
[†]Institute fur Macromoleculare Chemie, Albert-Ludwigs Universitat, Freiburg, D-79104, Germany
[‡]Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA
[§]Courant Institute of Mathematical Sciences, New York University, N Y NY 10012 USA

Liquid crystal elastomers (LCEs) are rubbers whose constituent molecules are orientationally ordered. Their salient feature is strong coupling between orientational order and mechanical strain[1]. Stretching or otherwise deforming an LCE sample changes the orientational order, which in turn changes bulk properties such as birefringence and dielectric susceptibility. Conversely, changing the orientational order gives rise to internal stress, which leads to strains that can change the shape of a sample. While orientational order can be affected by changes in temperature and other externally applied fields, light can also change the orientational order via a number of distinct processes. We demonstrate here that by dissolving azo dyes into an LCE sample, its mechanical deformation in response to visible light becomes large and very fast. Light induced bending of more than 60^o has been observed on the timescale of tens of milliseconds; this is more than two orders of magnitude faster than previous results.[2,3,4] Rapid light induced deformations allow LCE materials to interact with their environment in new and unexpected ways. We report here also the astonishing observation that when light is shined from above on a dye-doped LCE sample floating on water, the LCE "swims" away from the light.

I. Introduction

Mesogenic monomers incorporated into main- or side-chains of weakly cross-linked polymers can become orientationally ordered. The resulting LCE material combines the anisotropy and large susceptibility of low molecular weight liquid crystals with rubber elasticity. The possibility of coupling between orientational order and mechanical strain was first raised by de Gennes.[5] Symmetry arguments and free energy considerations indicate[1,6] that in nematic LCEs mechanical strain acts as an external field aligning the liquid crystal, while the orientational order acts as an external body stress, leading to elastic strain. The first LCE was synthesized by one of us[7] (H. F.). Recent interest in LCEs is fuelled both by their potential for device applications as artificial muscles[8] and mechanically tunable optical elements[9], and by curiosity regarding their unusual response to excitations[10,11].

In this work, we focus on the mechanical response of dye-doped nematic LCE samples to visible light. One effect is dye mediated heating due to absorption; the change in the degree of order caused by the change in temperature can lead to strain and shape change. Another is the reduction in the degree of orientational order due to photoisomerization of the dissolved dye. Liquid crystals can also be reoriented by light, with the required intensity dramatically reduced in dye-doped samples[12]. This anomalous reduction in the threshold intensity, the so-called Janossy effect, can be understood in terms of a Brownian ratchet mechanism, where the dye molecules in the nematic field are rotors of light-driven Brownian motors[13]. The optomechanical response of nematic LCEs with covalently bonded azo dyes has been studied recently[2]. These materials showed large isochoric contraction (by more than 20% of their original length) when irradiated with UV light, with relaxation times of the order of one hour.

II. Sample preparation

Our monodomain LCE samples consist of siloxane main-chain and mesogenic benzoic acid phenyl ester side-chain units (Fig. 1). Using a tri-functional cross-linker, samples under preparation are first weakly cross-linked, then stretched unidirectionally to align the mesogens and establish nematic order, and then finally fully cross-linked to form a transparent birefringent monodomain[14]. The alignment direction can be determined from the orientation of the principal optical axes. In order to retain high orientational mobility in our samples, the azo dye Disperse Orange I was dissolved (rather than functionalized as in Ref. 2) into the network.

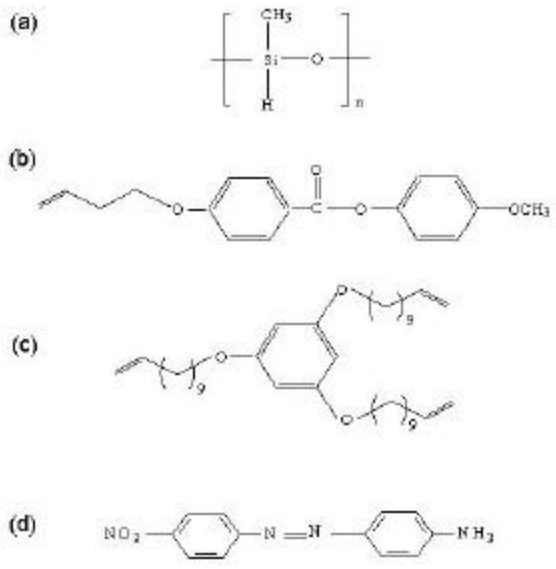


Figure 1. The chemical structures of the nematic LCE and dye: (a) the methylsiloxane monomer backbone; (b) the mesogenic benzoic acid phenyl ester side-chain; (c) the tri-functional cross-linker; (d) the azo dye Disperse Orange I.

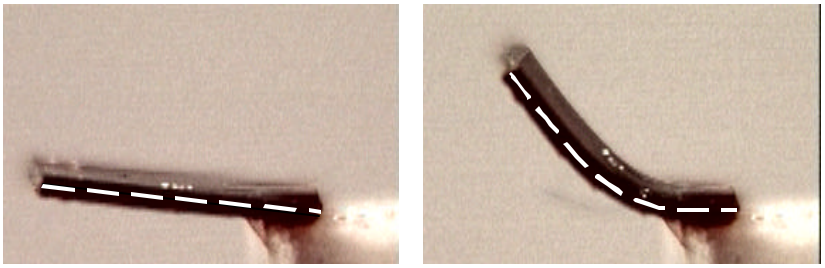
To accomplish this, nematic LCE samples were swollen with toluene in which the dye had been dissolved; the toluene was subsequently removed through evaporation in a vacuum oven. The concentration of the dye remaining in the samples, estimated from absorptivity measurements, was $0.1\ wt.\%$. The density of our samples is $0.973 g/cm^3$, and the thickness of the undeformed LCE films is $0.32 mm$. Disperse Orange I molecules are known to align with the nematic director in liquid crystals. In our samples, we observed a broad absorption peak whose amplitude was strongly polarization dependent, with an absorption maximum at $l_M = 495 nm$.

III. Light induced bending

We illuminated our dye-doped LCE samples by green light at λ=514nm from a CW Ar+ ion laser. For $5mm$ x $5mm$ x $0.32mm$ samples supported at one end (Fig. 2), the dominant effect is a large and fast light induced bend deformation ($>45^o$ bend angle after illumination for $60ms$ at $600mW$). The axis of the cylindrical bend is parallel to the sample surface and perpendicular to the nematic director. We measured the force developed by our dye doped samples when prevented from bending and found remarkably fast response times, with a rise time of $30ms$ at $600mW$ and a relaxation time of $75ms$. These times were determined from the measured exponential approach to saturation, and the likewise measured exponential decay after cessation of illumination. The size of deformation and its time-scales are also power dependent with more rapid onset to larger deformation with increased power (e.g. a 67^o bend angle after irradiation for $60ms$ at $1.3W$).

The observed bending is consistent with a rapid material contraction along the nematic director at the irradiated surface. This contraction is apparently volume conserving as it is accompanied by an expansion (small, given the aspect ratio of the sample) in the orthogonal direction. The contraction is consistent with decreased orientational order at the surface, relative to the anisotropically ordered rest state, which could lead to the observed material strains. Plausible candidate mechanisms underlying this effect are laser heating by linear absorption and the reduction of orientational order by photoisomerization of the dye. Direct and indirect optical torques may also contribute. We are presently conducting further experimental and modeling studies to identify the salient mechanisms.

(a)



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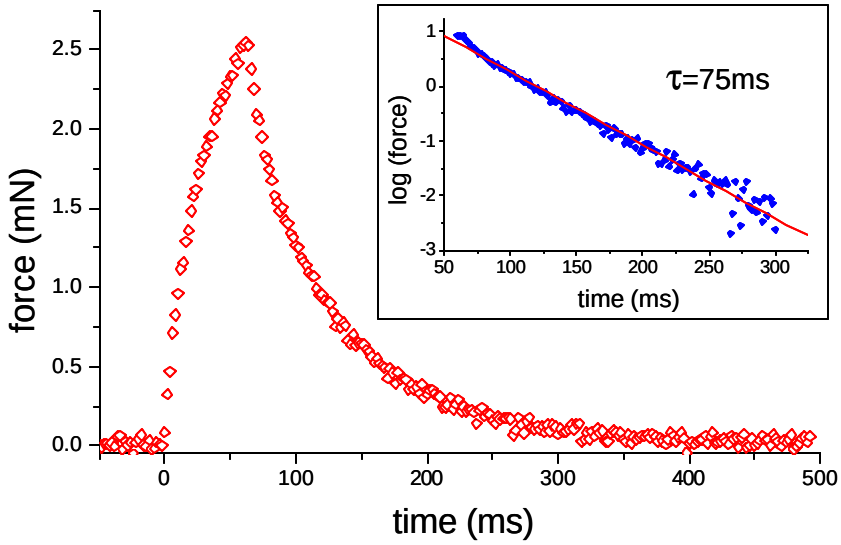
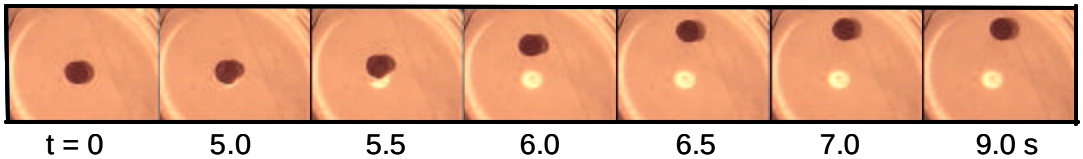


Figure 2. The opto-mechanical response of an LCE sample: (a) Two frames from a video clip recording the bending/relaxation dynamics of the sample. A 5 *mm* x 5*mm* x .32*mm* dye-doped LCE sample anchored at one end (left figure) is illuminated from above for 60*ms* by green light at ?=514 *nm* from a CW Argon$^+$ ion laser (600*mW*) with a 3*mm* beam waist (full width at half maximum). The Gaussian beam is approximately centered on the sample. (b) the sample 80*ms* after onset of illumination. The deformation has reached a bend angle of approximately 45^o. The dashed white line graphically superimposed on sample edge in the video image shows the orientation of the nematic director, and bending of the material due to contraction along the director. (b) the dynamics of force produced by the sample upon and subsequent to illumination for a 60*ms*. The free end of the sample was held in place and prevented from bending by the needle arm of an Entran™ load sensor measuring the force. The rise time of 30*ms* was determined by fitting the data in the increasing part of the force curve to an exponential approach to saturation. The inset shows the logarithm of the measured force after illumination is removed (60*ms* after onset). This reveals a clear exponential relaxation back to the rest state. The relaxation time, from the linear fit, is 75*ms*.

IV. Swimming into the dark

Finally, desiring to see how dye doped LCE materials might interact with their environment, we have studied their interaction with fluids by illuminating from above LCE samples floating on water. We find, astonishingly, that samples will swim away from the light. Fig. 3a shows video frames, while Fig. 3b. shows the position, of a 5*mm* diameter LCE disk under illumination with peak intensity of $1.1 W/cm^2$ from the Ar^+ ion laser.

(a)



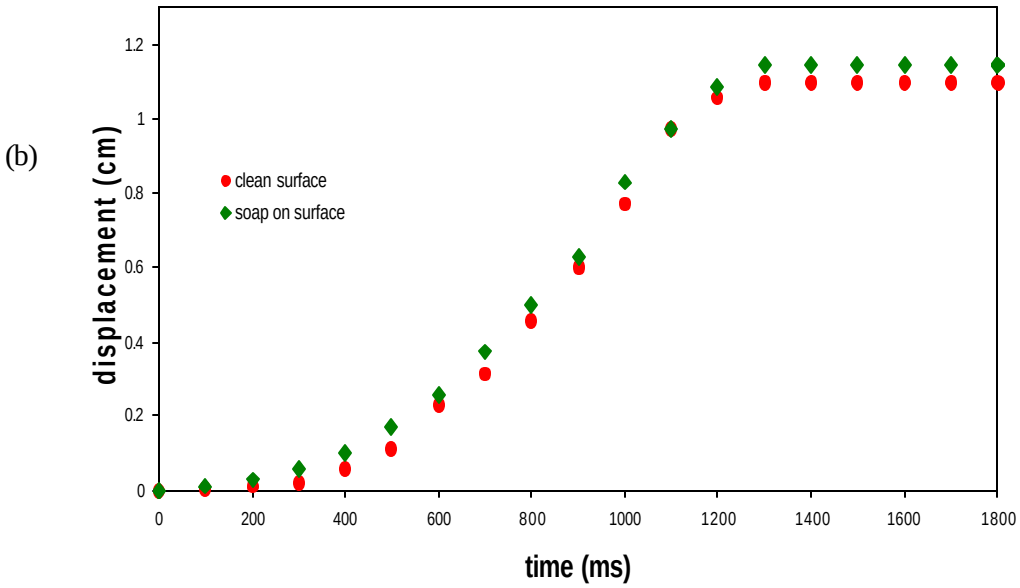


Figure 3. The interaction of a dye-doped LCE sample with a liquid. A 5*mm* diameter disk of dye doped LCE sample (.32 *mm* thick) is floating nearly motionless on the surface of water (approximately 2*cm* in depth) when illuminated from above by an Argon$^+$ ion laser with peak intensity of 1.1W/cm^2 and beam waist of 3 *mm*. (a) a series of video frames showing the LCE sample moving away from the area of sustained illumination (seen as the bright disk in the center). (b) the measured displacement of the LCE sample center from its initial rest position as function of time from onset of illumination. Since the motion is essentially the same in the presence of a surfactant soap (green) as on pure water (red), the motion does not originate in surface tension effects.

This swimming behaviour is remarkable since no linear momentum is transferred from the radiation field to the sample in the horizontal direction of motion. The system is therefore a motor, where motion is caused by the transfer of energy, but not momentum, to the system. We propose the following explanation for the observed swimming behaviour.

Energetics

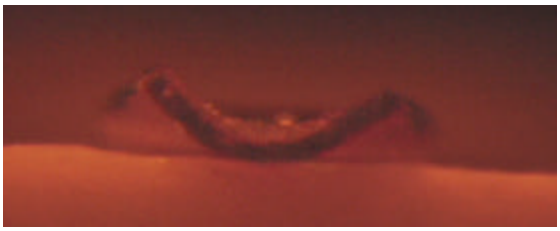
Regarding the energetics, we note that illumination causes the flat sample to change shape and to adopt a more compact, bent, configuration. On the cessation of illumination, the sample unbends to resume its original flat shape; it is capable of doing work in this process. Since the elastic energy of a bent elastic sheet is $\frac{1}{24} Y \frac{d^3}{R^2} A$, where Y is Young's modulus, R is the radius of curvature, d is the thickness and A is the area, a crude estimate of the energy stored in the bent sample is $\sim 10nJ$. When the sample adopts its compact configuration, it also sinks lower in the water. Since the potential energy of the water supporting the sample is Mgh, where M is the mass of the sample, g is the acceleration of gravity and h is the average depth of the sample under water, this shape change increases the potential energy of the water. A simple estimate of the potential energy, assuming a spherical deformation with radius of curvature equal to the disk diameter, gives $8nJ$. Energy for the swimming, provided by the light, is therefore stored both in the LCE and in the water. Since the sample shape depends on illumination which is localized, the sample

shape, and hence the potential energy of the system is a function of sample position. As the sample moves away from the light, it relaxes, regains its extended configuration, and makes available stored potential energy to do work and to cause motion. If one half of the stored energy provides the kinetic energy of motion and one half is dissipated in viscous shear, and one half of the kinetic energy is imparted to the water and the other half to the disk, the corresponding disk velocity is $\sim 4 cm/s$. This is the same order of magnitude as the observed maximum velocity of $1.9 cm/s$. Estimates of the exponential growth and decay times of the velocity are similarly in crude agreement with observations.

Momentum transfer

Regarding momentum transfer between the LCE sample and water during swimming, we conjecture the following scenario for the propulsion. If the illuminating beam is centered on the disk, the disk contracts along the director (and expands in the other two directions to conserve volume) forming a saddle shape, as shown in Fig. 4.

(a)



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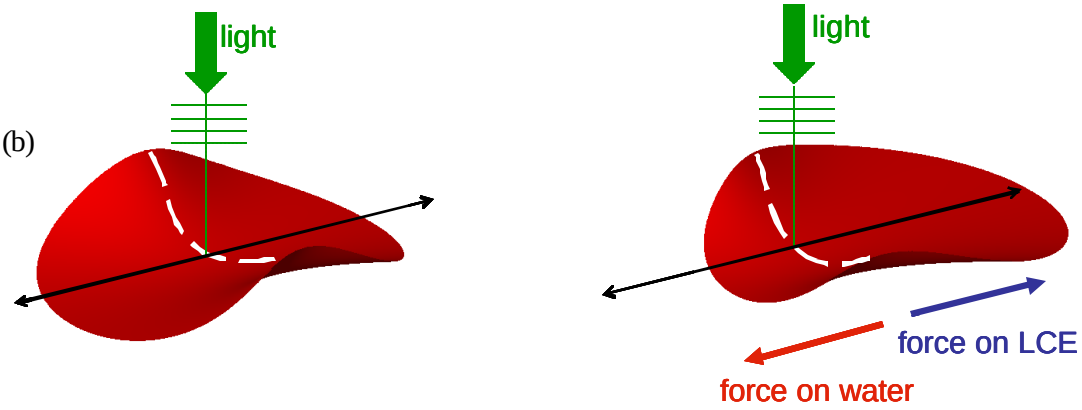

Figure 4. An image and schematic illustrating the mechanism underlying the locomotion of the dye doped LCE sample. (a) A single video frame showing the shape deformation of an LCE sample immediately following illumination. Here the sample sits on a dry surface and the image is recorded approximately along the axis of the bending, and hence orthogonal to the nematic director. This is the same shape deformation which occurs when the sample is floating on a liquid, further illustrated in (b). (b) schematic illustration of how the sample shape changes and how the sample interacts with the fluid

below. The figure on the left shows the initial deformation of the sample upon illumination. The black arrow shows the axis of the bend, which is orthogonal to the nematic director whose alignment direction across the sample is shown as a dashed white curve. The figure on the right shows the motion of the sample as the center of deformation moves back along the axis of the bend toward the light, and momentum is exchanged between the sample and the fluid

If the deformed disk is now slightly displaced (say by water or air convection currents, capillary waves or other noise) so that its center moves away from the laser spot in the direction normal to the director, the shape will change again, with the elevated "shoulders" moving in the direction opposite to the displacement, towards the stationary laser spot. This motion will push the water under the shoulders in same direction as the motion of the shoulders, in the direction opposite to the displacement, and, by Newton's third law, water will in turn push the LCE sample in the direction of the original displacement. The force from the water will accelerate the sample and lead to a further displacement in the same direction, resulting in yet greater force from the water. The original configuration with the illuminated sample under the beam is thus unstable; any in-plane perturbation of the sample position normal to the director gives rise to a force in the same direction, which, with increasing magnitude, will push the sample from under the illuminating beam. The stationary LCE sample under the light is therefore at an unstable fixed point; a perturbation in position or velocity will cause it to escape in the direction normal to the director. The geometric shape of the undeformed flat sample does not appear to be critical for swimming, we have observed similar behaviour with rectangular as well as irregularly shaped samples.

V. Discussion

The exchange of momentum between water and floating object is the basis of rowing, which can be dominated by either inertial or viscous effects. The Reynolds number of the water, estimated from the size and speed of the LCE sample, is approximately 100, indicating that both inertial and viscous forces are significant. The shape change dynamics is furthermore similar to that of a peristaltic pump; the pumping here, however, develops as part of the intrinsic dynamics moving the system away from an unstable equilibrium. Pushing water backward to move forward is also common in biological locomotion; water striders use depressions in the free surface of water as oars and to "row" across the surface[15]. We envision similarly sustained, but optically driven locomotion of an LCE sample by tracking and periodic illumination; drive schemes other than light (thermal, electrical, magnetic) that induce controlled shape changes may also be viable.

VI. Summary

Nematic LCEs with dissolved rather than functionalized azo dyes undergo large and fast shape changes on illumination. Samples floating on water swim away from the light, since the compact deformed configuration increases the energy of the system. We conjecture that if the illuminated configuration was the extended non-compact shape, the samples could swim towards the light. Key to the swimming process is the position dependent shape change. The floating LCE sample and the supporting fluid constitute an

unusual motor; the light source must supply not only energy, but also positional information, to bring about motion. Detailed modelling of the dynamics of this system, combining the statistical mechanics of LCEs[6] with the generalized hydrodynamics of viscoelastic solids[16] is currently under way.

Acknowledgements

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